

Bolin Gong · Yan Wang

ICP-AES determination of traces of noble metal ions pre-concentrated and separated on a new polyacrylacylaminothiourea chelating fiber

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Abstract A new polyacrylacylaminothiourea chelating fiber was synthesized simply and rapidly from nitrilon (an acrylonitrile-based synthetic fiber) and aminothiourea. This fiber was used for the pre-concentration and separation of traces of Au^{III}, Pt^{IV}, Pd^{IV}, and Ir^{IV} ions from aqueous samples. Factors effecting and parameters for the adsorption of these ions onto the resin, such as acidity, rate, reuse, capacity, and interference of other ions, were investigated using inductively-coupled plasma atomic emission spectrometry (ICP-AES). Conditions of desorption of these ions from the resin were similarly investigated. The enrichment factor was 100. The relative standard deviation for the determination of Au^{III}, Pt^{IV}, Pd^{IV}, and Ir^{IV} were in the range of 0.7–3.0% for 20.0 ng/mL of each. The recoveries of a standard from real solution samples were between 96% and 100%. The concentrations of analyzed ions in a digested metal powder sample processed with the method proposed were in good agreement with the certified values.

Keywords Noble metal traces · ICP-AES · Pre-concentration · Polyacrylacylaminothiourea fibers

Introduction

The separation and pre-concentration of traces of noble metals by means of macroporous resins [1, 2, 3, 4, 5, 6, 7, 8, 9] or chelating fibers [10, 11, 12, 13] have been reported. However, the majority of macroporous resins suffer from a slow rate of enrichment of metal ions [1, 2, 3, 5, 6, 7, 8, 9]. The chelating fibers typically have low ca-

pacities and desorption of noble metals from the fibers is usually difficult. The synthesis of chelating resins or fibers is often time consuming and complicated. In this paper, we report a one-step synthesis of a new polyacrylacylaminothiourea chelating fiber from nitrilon and aqueous aminothiourea (thiosemicarbazide). The properties of the chelating fiber for the pre-concentration and separation of traces of Au^{III}, Pt^{IV}, Pd^{IV}, and Ir^{IV} from aqueous samples were studied in detail using ICP-AES. The precision and accuracy of the proposed method were checked by the analysis of a real sample solution and a digested powder sample with satisfactory results.

Experimental

Instruments and apparatus

An ICP/6500 inductively-coupled plasma emission spectrometer (Perkin-Elmer), a model 170-sx Fourier transform IR spectrometer (Nicolet), a model 1106 Elemental Analyzer (carlo Erba) and a Model pHs-3A digital pH meter (Analysis Instrument Factory, Beijing, China) were used. A three-necked flask with a stirrer, thermometer, and spherical condensate were used for the synthesis of the chelating fiber. The adsorption column was an internally tapered glass tube of 15 cm length, 0.5 cm i.d., and 0.2 cm i.d. at the lower end with a stopcock to control the flow rate. A small pad of cotton wool was placed in the column and it was then filled with 0.1 g of the polyacrylacylaminothiourea chelating fiber which had been soaked overnight in distilled water. The conditions for ICP-AES spectrometer were: quartz torch; cross-flow nebulizer, forward power 1100 W; viewing height 15 mm; Ar plasma gas flow rate 15 L min⁻¹; Ar nebulizer gas flow rate 1.0 L min⁻¹; Ar auxiliary gas flow rate 0.7 L min⁻¹; solution uptake rate 1.0 mL min⁻¹; integration time: Au 10 s, Pt 10 s, Pd 10 s, Ir 10 s; 5 replications; wavelengths: Au 242.795 nm, Pt 214.423 nm, Pd 248.892 nm, Ir 224.268 nm.

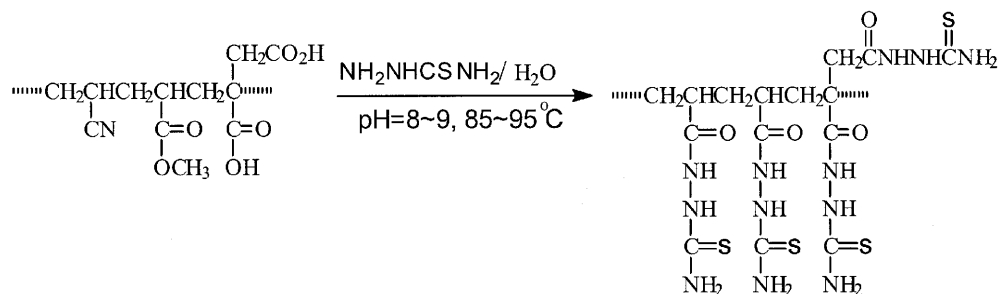
Reagents and standards

Nitrilon (Lanzhou Chemical Factory) was cut to 1.0 cm length, washed with ethanol and distilled water, and dried under an infrared drying lamp. Reagents of spectral and analytical purity were used for all experiments. Aminothiourea-HCl (99%) was purchased from Beijing Reagent factory. The other chemicals such as HCl, NaOH, CS(NH₂)₂ were purchased from Shanghai Reagent factory.

B. Gong (✉)
Department of Chemistry, Ningxia University,
Yinchuan, 750021, China
e-mail: gongbl01@263.net

Y. Wang
Institute of Modern Separation Science, Northwest University,
Shaanxi, Xi'an, 710069, China

Scheme 1



The stock solutions of 1.00 mg mL^{-1} of the four ions were prepared according to [16]. They were diluted and mixed to give standard stock solutions containing $20.0 \text{ }\mu\text{g mL}^{-1}$ each of Au, Pt, Pd, and Ir in 1.0 mol L^{-1} HCl and the standard stock solutions were used for all experiments.

Synthesis and characterization of the chelating fiber

A 30 g portion of dried nitrilon (containing 93% acrylonitrile, 5.7% methyl acrylate, and 1.3% itaconic acid) and 150 g of an aqueous 45% aminothiurea (thiosemicarbazide) solution were placed in a three-necked flask. The mixture was adjusted to pH 8–9 with NaOH solution, and refluxed for 12 h at $85\text{--}95^\circ\text{C}$ with slow stirring. The product was washed with distilled water until neutral and then dried under IR irradiation to obtain a gold-colored polyacrylaminothiourea chelating fiber. The nitrogen content of the fiber was 29.5% as determined by the Kjeldahl-Gunning method. The structure of the chelating fiber was analyzed by Fourier transform infrared spectroscopy (FTIR) [14, 15]. The synthesis is summarized in Scheme 1.

Analytical procedure

The mixed standard solutions of Au, Pt, Pd, and Ir or the real sample solutions were transferred by pipette into beakers ($100\text{--}1000 \text{ mL}$). The solutions were adjusted to pH 2 with aqueous ammonia or dilute HCl solutions and passed through the adsorbing column at a flow rate of 20.0 mL min^{-1} . The analytes were eluted with 15 mL of $4 \text{ M HCl} + 3\% \text{ CS}(\text{NH}_2)_2$ solution (at 70°C) at a flow rate of 5.0 mL min^{-1} . The ions in the 15 mL of eluate were then determined by ICP-AES under standardized conditions.

Results

Influence of HCl concentration on adsorption

Mixed standard stock solutions containing 20.0 ng mL^{-1} each of Au, Pt, Pd, and Ir ions were concentrated using the column procedure described in the range $10^{-5}\text{--}2 \text{ M}$ HCl. The results showed that traces of Au and Ir (at $1.0\text{--}10^{-5} \text{ M}$), Pt (at $10^{-1}\text{--}10^{-5} \text{ M}$), and Pd (at $10^{-2}\text{--}10^{-3} \text{ M}$) could be enriched quantitatively by the fiber with recoveries $>95\%$; recoveries of all elements were higher than 97% at 10^{-2} M . In order to determine these elements simultaneously, pH 2 was selected.

In addition, at pH 2: K, Na, Ca, Mg, Ni^{II} , Cu^{II} , Co^{II} , Mn^{II} , Ga^{III} , and As^{III} (As^{3+}) were not adsorbed on the fiber column; La^{III} (La^{3+}), Hg^{II} , Cd^{II} , and Pb^{II} were adsorbed only at 15–45%; Ru^{IV} and Rh^{IV} were enriched by 60–70%. However, because the fiber adsorbs Au, Pt, Pd, and

Ir ions strongly, their enrichments were not influenced by these other ions.

Effect of flow rate on enrichment

When the recommended procedure was used, the flow rate for pre-concentration of the analytes on a fiber column at pH 2.0 varied between 5.0 and 35.0 mL min^{-1} . The results showed that Au, Pt, Pd, and Ir ions could be enriched quantitatively at a flow rate of 23.0 mL min^{-1} with recoveries of 94.5%. 20.0 mL min^{-1} was selected as the pre-concentration flow rate.

Conditions for elution

After traces of Au, Pt, Pd, and Ir were enriched on the fiber column, the analyte ions were eluted with dilute HCl or $\text{CS}(\text{NH}_2)_2$, respectively. However, the recoveries of Au, Pt, Pd, and Ir ions eluted in this way were only 70–80%. In order to achieve complete desorption of the analytes from the fiber column, varying concentrations of the HCl and $\text{CS}(\text{NH}_2)_2$ used and the desorption flow rate were tested for 15 mL eluate volumes. The results showed that the Au, Pt, Pd, and Ir ions concentrated by the fiber columns could be desorbed quantitatively with 15 mL of $4 \text{ M HCl} + 3\% \text{ CS}(\text{NH}_2)_2$ solution at a flow rate of 5.0 mL min^{-1} , with recoveries $>97\%$. However, HCl concentrations above 4 M decreased the ICP-AES results by about 10%, because the viscosity and surface tension of the eluted solutions were increased, resulting in lower nebulization rates of the elutes compared to the standard solution.

Adsorption capacity and reuse of the fiber

0.1 g portions of the fiber were placed in each of the four conical flasks. A stock solution of each of Au, Pt, Pd, and Ir ions was added to each flask and diluted to 100 mL . The acidity of each solution was adjusted to pH 2 with aqueous ammonia or dilute HCl, and the vessels were shaken in a mechanical vibrator. The concentrations of the above ions in solution were measured at 10 min intervals by ICP-AES until equilibrium was reached. In this way the saturation adsorption capacity of the fiber was calcu-

Table 1 Interference of other ions on analyte recoveries

Interfering ions Conc ($\mu\text{g mL}^{-1}$)	Ca ^{II} (50)	Mg ^{II} (50)	Fe ^{IIIb} (50)	Al ^{IIIb} (50)	Zn ^{II} (50)	Cu ^{II} (50)	Mn ^{II} (30)	Ni ^{II} (30)	Cd ^{II} (30)
Recovery ^a (%)									
Au	98.5	99.0	96.5	95.0	98.5	98.5	100	98.0	96.0
Pt	99.4	99.0	95.5	96.0	98.5	98.5	99.0	100	97.8
Pd	100	100	96.0	94.5	97.5	96.0	95.5	100	95.0
Ir	98.0	97.5	95.5	97.0	100	98.5	98.0	97.0	96.0

^aThe concentrations of Au^{III}, Pt^{IV}, Pd^{IV}, and Ir^{IV} were 50 ng mL⁻¹ each

^bAl^{III} was masked with 0.1 g citric acid, Fe^{III} (or: Fe³⁺) was masked with 0.1 g of hydroxylamine hydrochloride (NH₂OH.HCl)

lated as 2.80 mmol g⁻¹ for Au^{III}, 1.75 mmol g⁻¹ for Pt^{IV}, 1.56 mmol g⁻¹ for Pd^{IV}, and 1.15 mmol g⁻¹ for Ir^{IV}.

When the fiber was used repeatedly (up to 10 times) as described for the enrichment and determination of Au, Pt, Pd, and Ir ions (after these ions were desorbed from the fiber each time with 15 mL of 4 M HCl + 3% CS(NH₂)₂, the fiber column was washed to neutrality with distilled water), the adsorption efficiency was still >92%. The chelating fiber did not display obvious signs of swelling effects after being used for 10 times.

Interference of other ions

Different potential interfering ions were added to dilute analyte standards. The analytes were pre-concentrated and determined as described above. The results, summarized in Table 1, show that an excess of a hundred to a thousand times of these ions caused little interference in the determination of the analytes. Various other precious and heavy metals present (e.g., Os, Ag, Ru, Rh, Cd, Hg, Bi, and and Tl) did not interfere with the analytes either because their concentrations in real samples were very low or the rates at which they were adsorbed by the fiber were much lower than the adsorption rates of the analytes.

Analytical precision and accuracy

Under the selected conditions, the recoveries of traces of 20.0 ng mL⁻¹ each of Au, Pt, Pd, and Ir in 1000 mL of solutions, enriched and determined simultaneously seven times, were in the range 97–100%. The relative standard deviation (RSD) was between 0.7% and 2.6%.

Table 2 Analytical results of a real sample solution with non-ferrous metal matrix^a

Element	Concentration (ng mL ⁻¹)			Recovery (%)	RSD (%)
	Found (n=5)	Added	Sum (n=5)		
Au	30.5±0.5	50.0	80.0±0.8	99.0	3.0
Pt	115.0±2.0	50.0	164.0±2.5	98.0	2.1
Pd	49.0±1.0	50.0	98.0±1.6	98.0	2.5
Ir	45.0±0.7	50.0	93.5±1.2	97.0	2.7

^a0.1 g citric acid and 0.1 g NH₂OH.HCl added

Table 3 Analytical results of digested powder sample solution

Element	Concentration (%)		
	Certified ^a	Found ^b	RSD (%)
Au	0.320	0.318	3.2
Pt	0.650	0.640	2.3
Pd	0.380	0.375	2.7
Ir	0.330	0.327	3.0

^aThe results obtained by the smelter laboratory using high-temperature electrothermal atomic absorption spectrometry

^bAverage of five determinations

The accuracy of the combined pre-concentration-ICP procedure was checked by analyzing a real aqueous sample obtained from a non-ferrous metal smelter (500 mL of the real aqueous sample was filtered. 100 mL of the filtered solution was diluted to 1000 mL with distilled water and adjusted to pH 2. Then 10 mL of this diluted solution was analyzed according to analytical procedure) using the standard addition method. The results in Table 2 show that the recoveries of Au^{III}, Pt^{IV}, Pd^{IV}, and Ir^{IV} ions added to the sample were in the range 97–99%, RSDs were in the range 2.1–3.0%. In addition, a 0.1000 g portion of a powdered non-ferrous metal sample (containing Zn, Ni, Cu, Cd, Mn, Fe, Al, Ca, and Mg matrix elements) from a smelter was weighed and put into a Ni crucible to which 0.3 g of Na₂CO₃ and 1.0 g Na₂O₂ were added. The crucible was heated in a furnace for 7 min at 750 °C and then cooled. The melted sample was leached with 30 mL of boiled distilled water into a beaker, to which 30 mL of 12 M HCl was added with stirring. The solution was heated for 30 min until it becomes transparent. The solution was diluted to 1000 mL with distilled water and was adjusted to pH 2 with aqueous ammonia. 10 mL of this solution was then analyzed according to the analytical procedure and the results are given in Table 3. It can be seen that the results are in good agreement with the certified values obtained by the smelter laboratory using high-temperature electrothermal atomic absorption spectrometry.

Conclusion

A new polyacrylaminothiourea chelating fiber with a high adsorption selectivity for Au^{III}, Pt^{IV}, Pd^{IV}, and Ir^{IV}

ions was synthesized in a simple and economical fashion. Merits of the fiber are lower interference, higher adsorption capacity, better reuse ability and higher chemical and mechanical stability than reported fibers and methods [10, 11, 12]. Pre-concentration by this fiber combined with ICP-AES can be applied to the determination of trace amount of Au^{III}, Pt^{IV}, Pd^{IV}, and Ir^{IV} ions in solution samples from a metal smelter and digested powder samples with satisfactory results.

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